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Research paper

Stability, lability, spectral parameters and structure of complexes and stereoselective effects in the nickel(II) – L/D/DL-histidine – L/D/DL-methionine systems

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ABSTRACT

The equilibrium constants, spectral characteristics of complexes, formation thermodynamic parameters and constants of the chemical exchange reactions in the nickel(II) – L/D/DL-histidine (HisH) – L/D/DL-methionine (MetH) systems (25 °C, 1.0 mol dm^{-3} KNO_3) over wide ranges of pH and ligands to metal ratio were calculated from the pH-potentiometry, multi-wavelength electronic spectroscopy, calorimetry and NMR relaxation data. Based on the DFT computation the structures of some complexes have been proposed. Significant enantioselective effects are exhibited in the formation constants and in some electronic spectra and NMR relaxation parameters of a number of complexes with the *meso*-forms domination. For the $Ni(His)_2$ complex the process of alkaline catalysis of proton exchange with the short-time N-H proton removal from the coordinated imidazole fragment was characterized. It was shown that in the ligand exchange reaction between $Ni(His)_2$ and His^- the $Ni(His)_3^-$ complex participates as an intermediate. It was found that the Met^- thiomethyl group is not bounded in the $Ni(Met)^+$ and $Ni(Met)_2$ complexes but coordinated in the Ni(His)(Met) form. Main factors determining stereoselectivity in the complex formation processes and ligand exchange reactions in the systems studied were identified as *trans* effect, solvation effect and a new type of interligand thiomethyl group–imidazole ring weak interaction.

1. Introduction

Understanding the causes of specificity and selectivity of processes in nature is one of the most actual problems of modern science. Solving this problem requires a study of objective laws of complex formation processes that are common in biological systems. In this relation it is useful to compare the stereoselectivity parameters of complex formation in the rows of both biometals and bioligands including amino acids. Of special importance is investigation of the histidine (HisH) metal complexes because they are involved in the biological metal transport [1] and because the histidine residue enters into the composition of active centers of many metalloenzymes [2]. It is extremely important that methionine (MetH) residues can serve as endogenous antioxidants in proteins [3], theirs oxidation up to the methionine sulfoxide leads to neurodegenerative processes including Alzheimer's and Parkinson's diseases [4] and these reactions can occur with participation of metal-bound oxidants [5]. The most attention deserves heteroligand complexes of metals with amino acids because of the wide variety of their properties and the prospects for their application in chemistry, biology and medicine [6].

In the first place it is necessary to compare in detail the homo- and heteroligand L/D/DL-histidine and L/D/DL-methionine metal complexes in the row of the neighbouring metal ions, nickel(II) – copper(II) – zinc(II). In the previous work [7] we have investigated the copper(II) – L/DL-histidine (HisH) systems in aqueous solutions on the 1.0 mol dm^{-3} KNO_3 background by pH-potentiometry, spectrophotometry, EPR and NMR relaxation methods with invoking computer modelling and quantum chemical computations. In the present work we have undertaken analogical investigation of the nickel(II) – L/DL-histidine systems. Complex formation of nickel(II) with histidine has been studied by many authors (see reviews [8,9]). However, stereoselectivity of complex formation in the

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